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SSMAS NMR STUDY OF HD, GD, AND VX ON CARBON FIBER TEXTILES FOR WIPES



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PREFACE

The work described in this report was authorized under Contract No. DAAD13-03-D-0017. The work was started in October 2005 and completed in December 2007.

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SSMAS NMR STUDY OF HD, GD, AND VX ON CARBON FIBER TEXTILES FOR WIPES

1. INTRODUCTION

Previous studies using SSMAS NMR have focused on the degradation of HD, VX, and GD on MgO,¹ CaO,² alumina,³ zeolites,⁴ and HD on soil.⁵ More recent studies have focused on the degradation of HD on concrete,⁶ asphalt, limestone⁷ and sand, and VX on concrete.⁸ This work measures HD, GD, and VX degradation on mesoporous and microporous carbon fiber textiles and compares the VX results to recently-obtained degradation rates on sand.

2. EXPERIMENTAL PROCEDURES

2.1 Carbon Fiber Textiles.

The carbon fiber textiles used were commercial samples manufactured by Charcoal Cloth International (CCI) (Houghton-le Spring, UK), a subsidiary of the Calgon Carbon Company (Pittsburgh, PA), and contain microparticles of ZnO on the surface⁹ (Table 1). The fiber textiles labeled "VIP" had vanadium pentoxide deposited upon them from aqueous solution by R. Kaiser. The Perfect Clean[®] fiber textile (Umf Corporation, Wilmette, IL) was a commercial sample of a polyester fiber textile, generally used as an eyeglass cleaner.

Table 1. Physical Properties of the Carbon Fiber Textiles

| | FM100 Meso | 50K |
|---------------------------------|---------------|---------------|
| Type | Carbon | Carbon |
| Surface Area, m ² /g | 1160 | 1480 |
| Total Pore Volume, cc/g | 0.75 | 0.72 |
| Micropore Volume, cc/g, <2 nm | 0.43 | 0.53 |
| Mesopores, cc/g, 2 – 50 nm | 0.32 | 0.19 |
| Pore size range | 0.45 – 1.4 nm | 0.4 to 1.6 nm |
| Process | Woven | Knit |

2.2 Agent.

The sulfur mustard was 50% ¹³C-labeled to get better NMR sensitivity, but the ¹³C were not adjacent to each other, to avoid ¹³C-¹³C coupling. In the abbreviation HD*, the term H represents sulfur mustard, D represents distilled, and * shows that the compound was ¹³C labeled. The VX was ton container (munitions) grade.

2.3 NMR Instrumentation.

The spectra were collected at 9.4 Tesla, using a wide-bore Varian Inova NMR spectrometer equipped with a Doty Scientific 7 mm supersonic VT-MAS probe using direct polarization, spinning rates of ~2000 Hz, and a 90° pulse width of 7.5 μ sec. The decoupler was not used as the conductivity of the carbon fiber textiles interfered with the signal. The silicon nitride rotors were packed with 17 mg fiber textile (12.8 μ L pore volume) or 200 mg sand, spiked with 4 μ L VX and optionally 8 μ L water (sand samples) using a microliter syringe, weighed, and sealed with Doty Scientific double O-ring Kel-F caps. The Delay times between pulses were at least five times the measured T_1 relaxation time. The ^{31}P spectra (VX, GD) were referenced to external phosphoric acid at 0 ppm,¹⁰ and ^{13}C spectra (HD) were referenced to external tetramethylsilane at 0 ppm.¹¹ This technique has been previously used and described.¹²

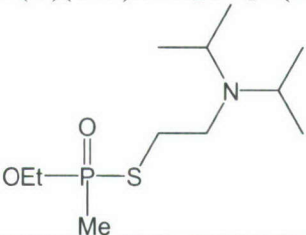
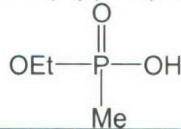
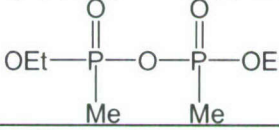
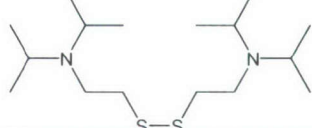
2.4 Gas Chromatography/Mass Spectrometry (GC/MS) and Liquid Chromatography/Mass Spectrometry (LC/MS) Instrumentation of VX Products.

Samples were screened by Gas Chromatography/Mass Spectrometry (GC/MS) and electro-spray Liquid Chromatography/Mass Spectrometry (LC/MS) for the presence of VX-related degradation products. The GC/MS characterization was performed using an Agilent 5973i MSD with splitless (1 min) injection. Conditions were as follows: 30m x 0.25mm HP-5ms column (0.25 μ m film) programmed from 50 °C (1 min) -280 °C at 15 °C/min ; injection temperature 250 °C ; transfer line temperature 280 °C; He flow rate 1.1 mL/min (constant flow); injection volume 1 μ L; and scan range 45-450 amu @ 1.86 scans/sec. The LC/MS screening was performed using a ThermoFinnigan TSQ-7000 LC/MS/MS equipped with a Phenomenex Luna 3 μ C18 150 x 4.6 mm column. The ionization mode was electrospray, spray voltage was 4.5V, capillary temperature was 200 °C, nitrogen sheath gas was 60 units, mobile phase was 50:50 methanol:50 mM NH_4OAc in water, flow rate was 0.25 mL/min, injection volume was 5 μ L, and the mass range was scanned from 90-400 amu @ 2 sec/scan. The compounds detected are listed in Table 2.

2.4.1 VX Quantitation for GC/MS and LC/MS.

The VX quantitation was performed using a linear external calibration curve with standards (0.126, 0.252, 0.504, 2.52, and 5.04 ng/ μ L) prepared by dilution of the provided 50.4 ng/ μ L reference solution. All dilutions were done in acetonitrile. Experimental GC/MS conditions were the same as the screening procedure except data was collected in the SIM mode using ions m/z 114, 139, 144, 167, and 193 (100 msec dwell time each ion). Quantitation was performed using the m/z 114 ion. The VX eluted at 11.59 min.

Table 2. VX and Degradation Compounds

| Compound | Structure |
|---|---|
| O-Ethyl S-(2-diisopropylamino)ethyl methylphosphonothiolate (VX) | $\text{MeP(O)(OEt)SCH}_2\text{CH}_2\text{N(iPr)}_2$  |
| Ethyl methylphosphonic acid (EMPA) | MeP(O)(OEt)OH  |
| O,O-Diethyl dimethylpyrophosphate (VX pyro, pyro) | $\text{MeP(O)(OEt)-O-P(O)(OEt)Me}$  |
| Bis-(2-diisopropylamino)ethyl disulfide (VX disulfide; RSSR, (DES) ₂) | $(\text{iPr})_2\text{NCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{N(iPr)}_2$  |

2.4.2 Bis-(2-diisopropylamino)ethyl Disulfide Quantitation.

The VX disulfide was quantified using the same method as for VX quantitation and eluted at 13.99 min under these conditions. A linear 3-point external calibration curve was obtained using 5.2, 10.4, and 20.8 ng/ μL standards prepared from a 1.040 mg/mL stock solution of VX disulfide. Quantitation was performed using the m/z 114 ion.

2.4.3 O,O-Diethyl Dimethylpyrophosphate Quantitation.

O,O-Diethyl dimethylpyrophosphate ("pyro") was quantified using LC/MS/MS. Experimental conditions were the same as for the screening technique except data was collected in the MS/MS mode. The parent ion was m/z 231, the daughter ion monitored was m/z 175, the collision energy was -15V, and the collision gas was Argon (1.9 mT). A linear 4-point external calibration curve was generated using standards at 0.5, 1.0, 2.5, and 5.0 ng/ μL . The 4-day sample was diluted 1:5 in acetonitrile prior to analysis.

2.4.4 EMPA Quantitation.

Ethyl methylphosphonic acid (EMPA) was quantified using the full scan GC/MS screening procedure and detected as the trimethylsilyl (TMS) derivative. Standards and samples were converted to the TMS esters by heating in the presence of BSTFA/1%TMCS for 45 min at 60 °C prior to analysis. EMPA standards at 2.5, 5.0, 10.0, and 25.0 ng/μL were prepared, derivatized, and analyzed to generate a linear 4-point external calibration curve (TIC used). Because VX pyro hydrolyzes to EMPA and also forms the TMS derivative, the values obtained for the samples represent the sum of the EMPA and VX pyro concentrations. The EMPA concentrations were obtained by subtracting the pyro concentrations detected by LC/MS/MS from the total EMPA + pyro concentration detected by GC/MS.

2.4.5 Sample Preparation.

The samples were prepared by spiking approximately 9 mg neat VX, TC grade onto 180 mg of the fabric. The fabric samples were first oven dried (120 °C) for 48 hr prior to use. The samples were extracted at the appropriate time with acetonitrile and then diluted for the LC/MS and GC/MS experiments.

3. RESULTS

3.1 Degradation of VX on Carbon Fiber Textiles.

3.1.1 Degradation of VX on Zorflex[®] FM 100 Meso Carbon Fiber Textile.

On the FM 100 meso fiber textile, the initial VX peak width was 110 Hz; subsequent peaks were ~400 Hz, indicating that the VX had entered the pores. The product was diethyl dimethylpyrophosphonate (“pyro”), which converted to EMPA after EMPA was added (Figure 1a). The ³¹P total integrated peak area showed that on ~60% of the anticipated signal was observed (Table 3). The kinetic plots (Figures 2 and 3) showed that VX loss was zero order with a first half-life of 100 hr; this was mirrored by the gain of “pyro” (Figure 3), suggesting that the conversion from VX to “pyro” was direct. The total integrated peak area decreased over time, suggesting that the agent absorbed into the fiber textile (Figure 4).

3.1.2 Degradation of VX on Zorflex[®] FM 50K Carbon Fiber Textile.

On the Zorflex FM 50K fiber textile, the VX (54 ppm) formed protonated VX (VXH⁺, ~60 ppm) and then a final product (26 ppm). EMPA (2 μL) added after the end of the reaction indicated that the product was “pyro,” not EMPA (Figure 1b). Good mass balance was maintained throughout the course of the reaction. The peaks were 50 to 70 Hz wide, indicative of a liquid-like state – that is, VX was on the surface of the fiber textile, not in the pores. Over the period of a week, the “pyro” reacted with the added EMPA to form more EMPA; the EMPA chemical shift moved due to the acid produced.

The kinetic plots showed that the total VX loss (VX plus VXH⁺) was first order with a half-life of 66 hr (Figure 5). However, the “pyro” formation was not first order due to the intermediate step of VXH⁺ formation in the reaction mechanism. The rates and orders of VX degradation on carbon fiber textiles were comparable with those observed on sand (Table 4). The mechanism for VX degradation is shown in Scheme 1 for fabric surfaces and in Scheme 2 for sand.

Munitions Grade VX on Zorflex FM100 Meso

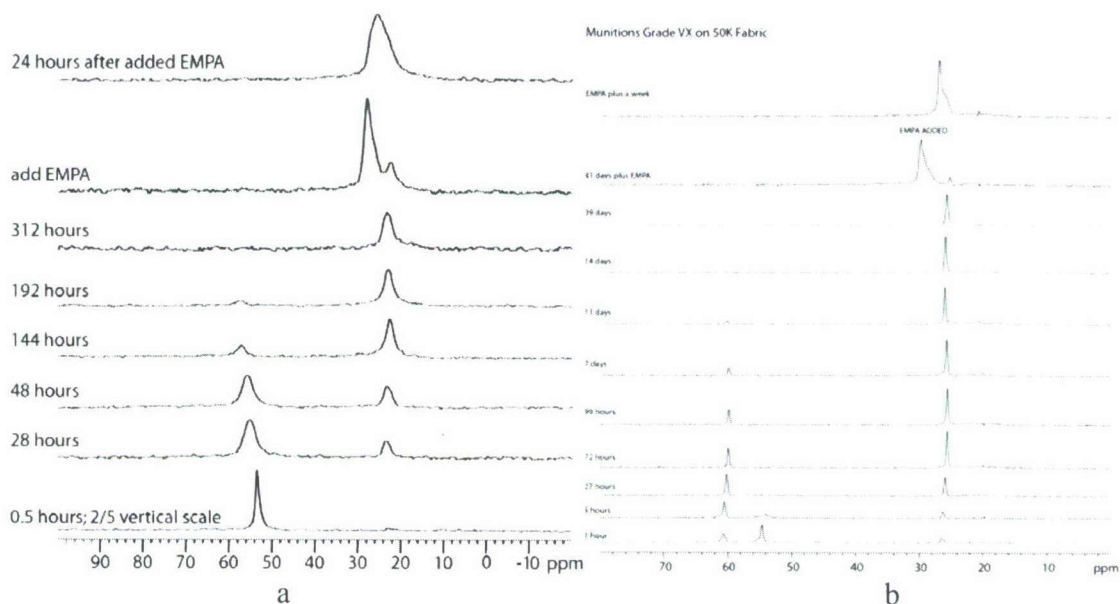


Figure 1. Degradation of VX on (a) Zorflex[®] FM 100 Meso and (b) 50K Fiber Textiles

Table 3. ³¹P Integral for VX, GD, and EMPA on a Variety of Substrates per Mole of ³¹P

| Substrate | Agent | Moles Agent | Initial integral /cm | Integral per mole ³¹ P /mm* | % ³¹ P observed |
|-----------|-----------|-------------|----------------------|--|----------------------------|
| 50K | GD | 0.0220 | 5.85 | 266 | 115 |
| 50K | VX | 0.0150 | 3.2 | 214 | 93 |
| 50K | VX & EMPA | 0.0182 | 6.4 | 209 | 91 |
| 100 Meso | GD | 0.0235 | 5.45 | 232 | 100 |
| 100 Meso | VX | 0.0155 | 2 | 129 | 56 |
| 100 Meso | VX & EMPA | 0.0132 | 3.2 | 141 | 61 |

*The average for 100% of the signal is 230 mm/mole ³¹P.

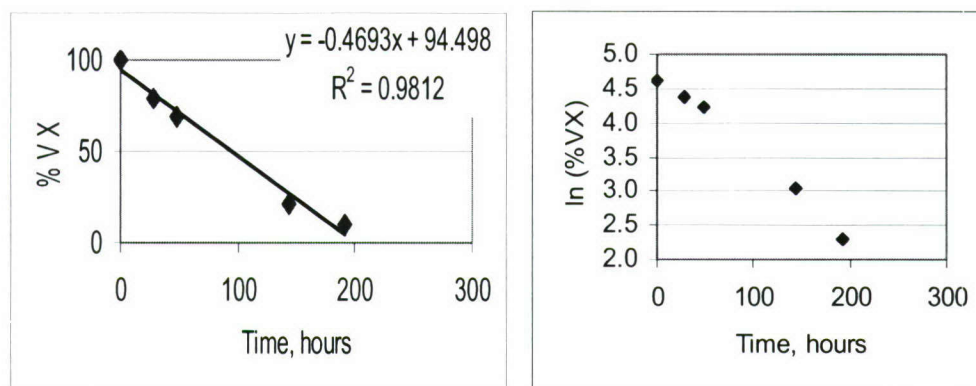


Figure 2. Zero and First-Order Kinetic Plots for VX Degradation on Zorflex® FM 100 Meso Fiber Textile

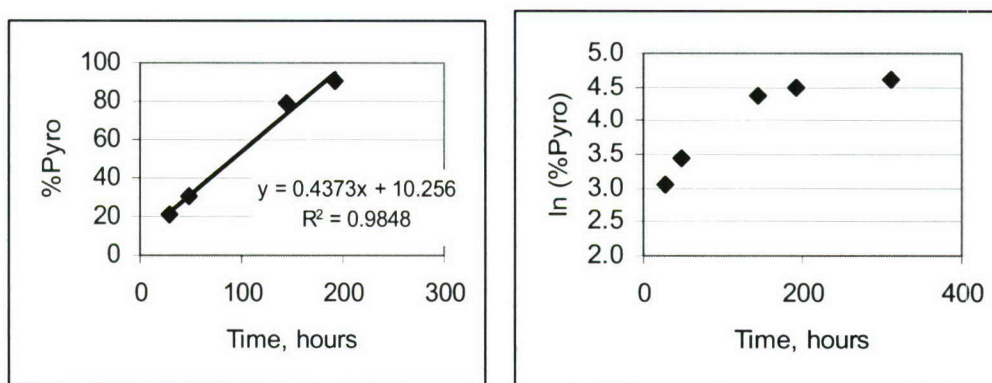


Figure 3. Zero and First-Order Kinetic Plots for "Pyro" Gain during VX Degradation on FM 100 Meso Fiber Textile

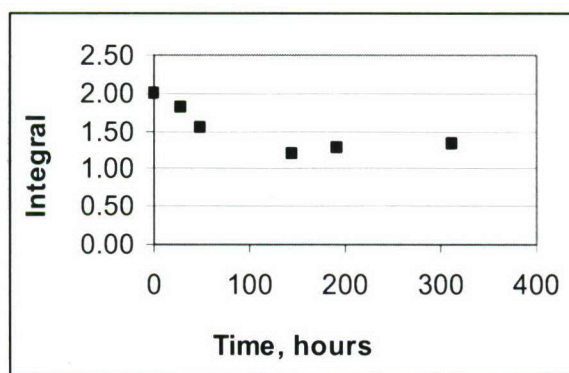


Figure 4. Total Integrated Peak Area for VX Degradation (Reactant and Products) on FM 100 Meso Fiber Textile

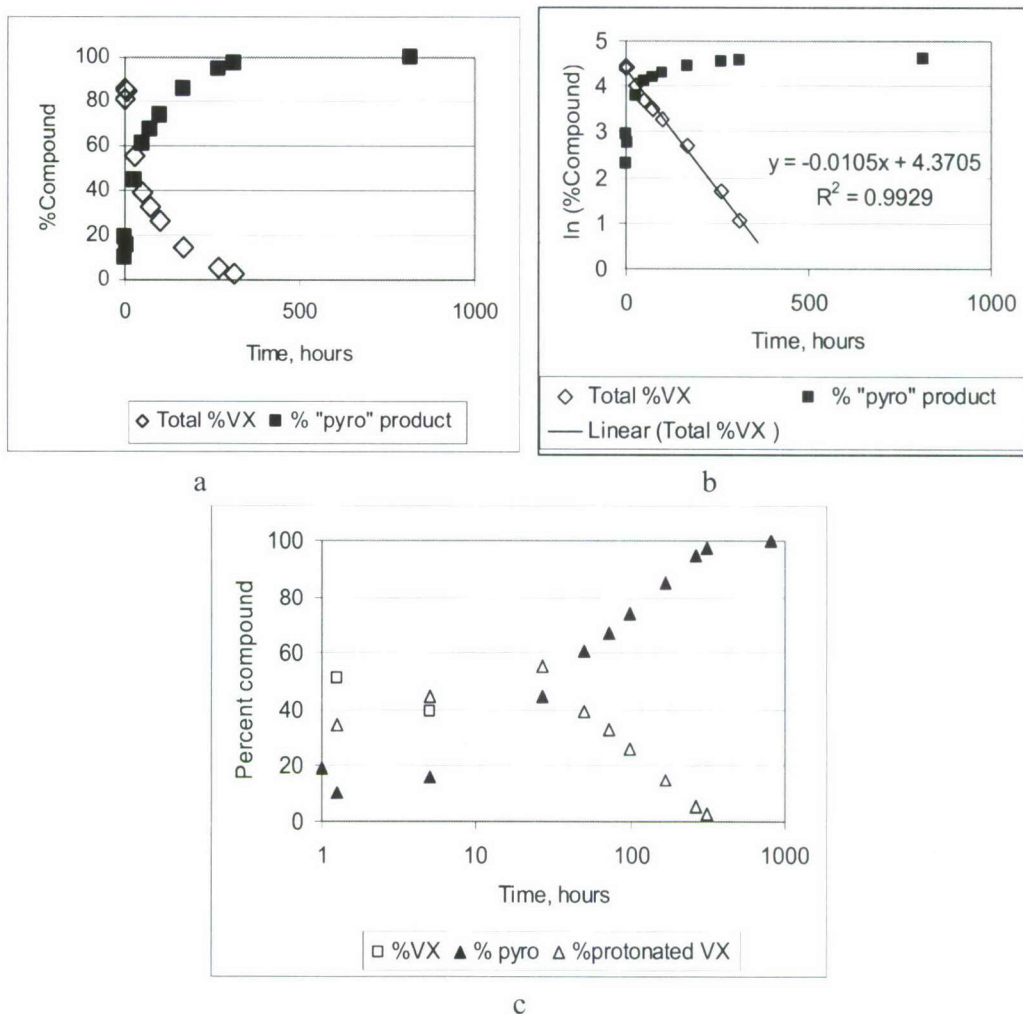


Figure 5. Zero (a, c) and First-Order (b) Kinetic Plots for VX Degradation and "Pyro" Gain on Zorflex® 50K Fiber Textile

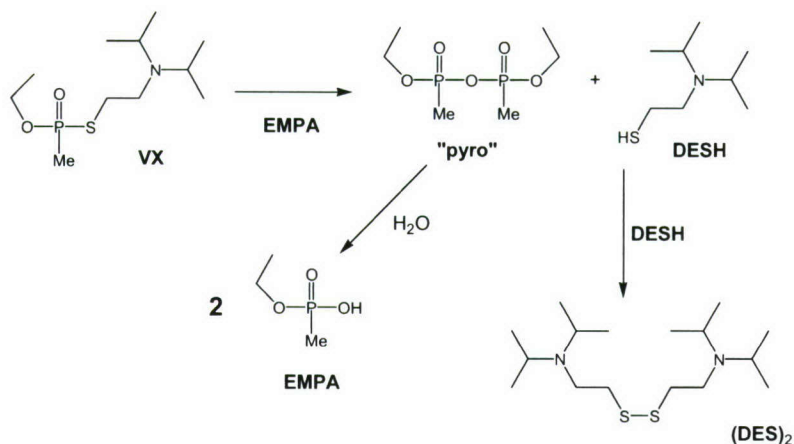
Table 4. Kinetic Results for Munitions Grade VX Degradation on Various Substrates

| Substrate | Water? | Order in VX | Half-life, h | % EMPA | % pyro | % EMPT | % EA2192 |
|-------------|--------|-----------------|------------------|--------|--------|----------------|----------------|
| 50K | No | 1 st | 66 | 0 | 100 | 0 | 0 |
| FM 100 Meso | No | 0 th | 100 ^a | 0 | 100 | 0 | 0 |
| UK Sand | No | 1 st | 43 | 100 | 0 | 0 | 0 |
| ME Sand | Yes | 1 st | 89 | 100 | 0 | 0 | 0 |
| UK Sand | Yes | 1 st | 223 ^b | 100 | 0 | 3 ^c | 9 ^c |

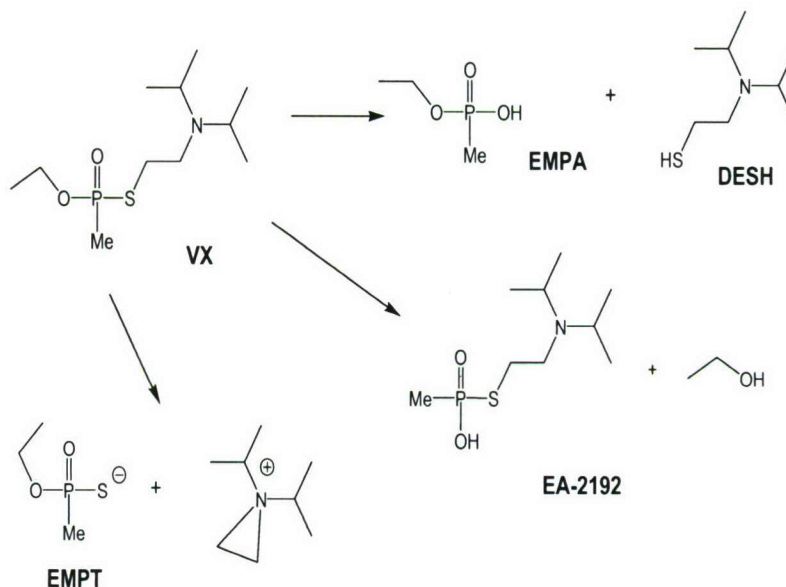
^aFirst Half-life.

^bThe half-life given is that for the Total VX (sum of VX and protonated VX).

^cThe EMPT and EA2192 are intermediates which degrade to EMPA.



Scheme 1. Mechanism for VX Degradation on Textile Fibers



Scheme 2. Mechanism for VX Degradation on Sand

3.1.3 Degradation of VX on Zorflex[®] FM 100 Meso Carbon Fiber Textile Detection via GC/MS and LC/MS.

A corroborating technique to the NMR experiments was extraction of sample and analysis of the extract via GC/MS and LC/MS. No methylphosphonic acid (MPA) or other products were detected. Quantitative results in Table 5 show that at 4 days VX and pyro were present. At 11 days, most of the VX had reacted, and the majority of the pyro had degraded to EMPA.

Table 5. GC/MS and LC/MS Quantitation of VX Degradation on Zorflex[®] FM 100 Meso

| Sample | VX (ng/ μ L) | EMPA (ng/ μ L) | Pyro (ng/ μ L) | (DES) ₂ (ng/ μ L) |
|---------|---------------------|-----------------------|-----------------------|-------------------------------------|
| 4 days | 3.0 | 1.7 | 14.7 | 13.0 |
| 11 days | 0.2 | 12.7 | 1.0 | 14.9 |

3.2 Degradation of Sulfur Mustard on Carbon Fiber Textiles.

3.2.1 Degradation of Sulfur Mustard on Zorflex[®] FM 50K Fiber Textile.

The degradation was measured using ¹³C SSMA S NMR for a sample that comprised 0.017 g fiber textile and 6.880 mg HD*. At 2 hr, small, sharp peaks indicated that not all of the mustard had absorbed into the pores (Figure 6a). The decoupler was turned off due to interference from the conductivity of the fibers; thus, the mustard peaks were a triplet due to coupling with ¹H, not a singlet. Broad peaks and a shorter T₁ indicated that mustard was in the pores (Figures 7a and 7b). The initial indication of product formation was seen at 13 days; at 6 weeks 40% sulfonium ion, HOEt-OT product (58, 53, 38, 22 ppm, 2:2:1:1) and 60% thiodiglycol (TDG) were present. The total integrated peak are decreased ~30% during the reaction; the initial decrease was the most rapid and represented the agent diffusing into the fabric (Figure 7c).

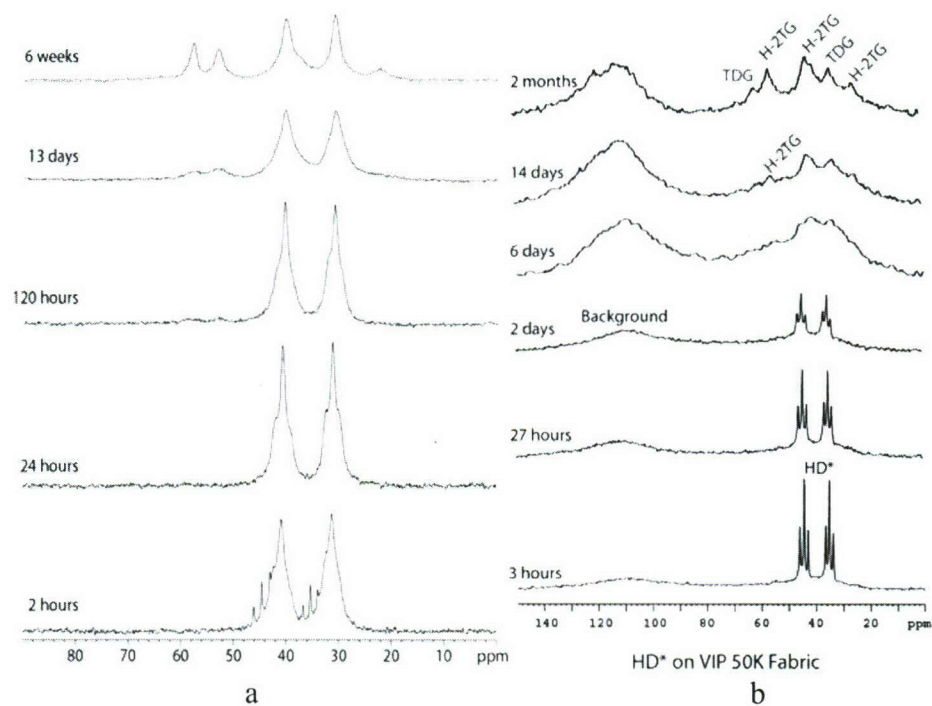
3.2.2 Degradation of Sulfur Mustard on V₂O₅-Coated Zorflex[®] FM 50K Fiber Textile.

The HD* adsorbed into the fiber textile immediately upon contact – no liquid HD* was seen in the rotor. The background at 110 ppm was constant; the later spectra were amplified compared to the first three. The HD* developed broader peaks, shorter T₁, lower signal intensity within 6 days, thus indicating that it had absorbed into the fiber textile (Figure 7). The spectra were not decoupled – the conductivity of the fiber textile interfered with the decoupling. Toxic H-2TG and non-toxic TDG were formed within 2 months. The rate observed was similar to that for the 50K fiber textile with no vanadia, thus, suggesting that the vanadium had no effect (Figure 6b).

3.2.3 Degradation of Sulfur Mustard on V₂O₅-Coated Perfect Clean[®] Polyester Fiber Textile.

The spectra, which were proton-decoupled, maintained the same shape for 1 month; peaks grew broader after 1 month, indicating absorption into the fiber textile. Over the period of 2 months, the T₁, total integrated peak areas and peak widths indicated that the HD* was merely adsorbed on the fiber textile for the first month; after a month the peaks began to broaden slightly, and the T₁s decreased slowly, indicating absorption (Figures 7a and 7b). The decrease in T₁ may also be due to interactions with the vanadium. The total integrated peak area was unchanged during

the period of study (Figure 7c). No reaction was seen; thus, neither the vanadia nor the fiber textile catalyzed the degradation rate (Figure 6c).



CB8-102B HD* on VIP PC

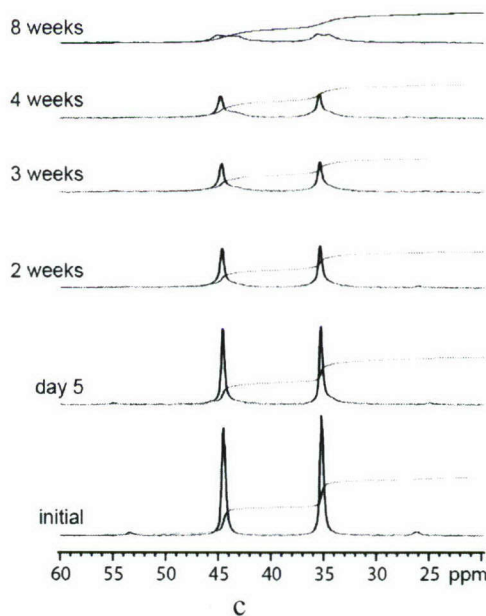


Figure 6. Degradation of HD* on (a) Zorflex[®] FM 50K Fiber Textile, (b) 50K Fiber Textile Coated with V₂O₅, and (c) "Perfect Clean" Fiber Textile Coated with V₂O₅

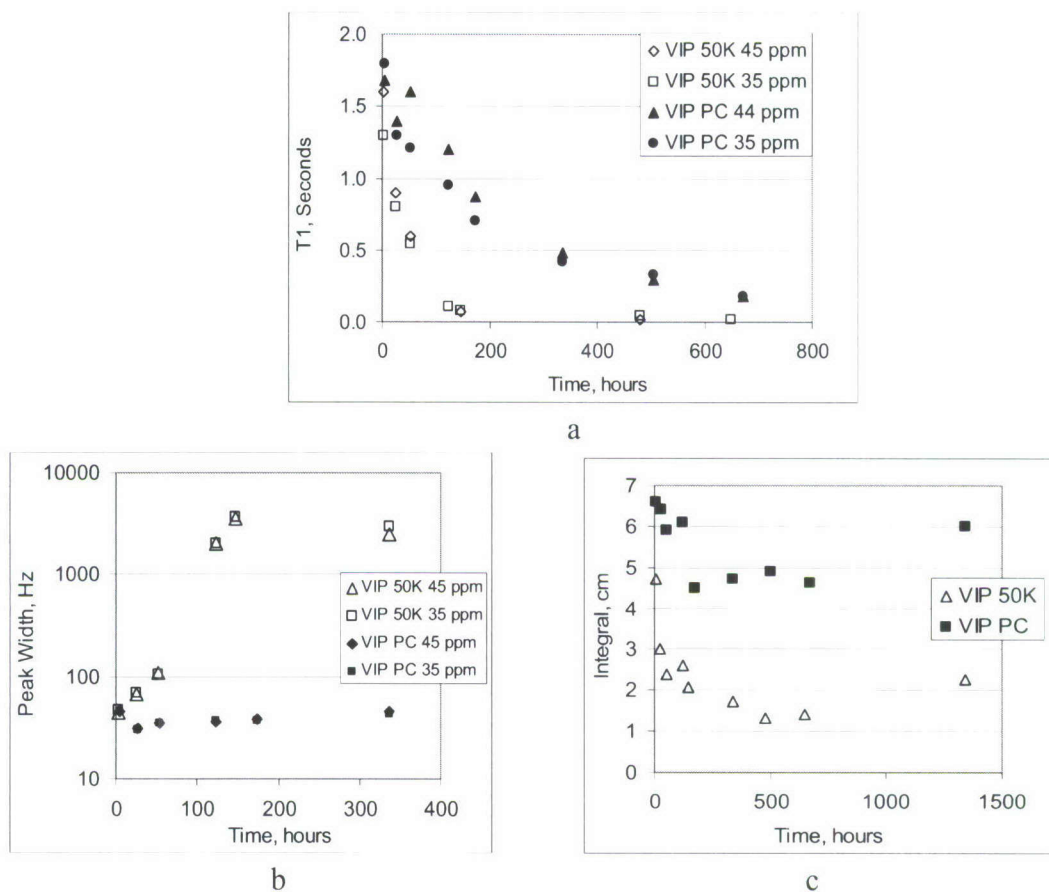


Figure 7. Evolution of (a) T₁ Relaxation Time, (b) Peak Width, and (c) Total Integrated Peak Area with Time for HD* on Vanadia-Coated 50K and "Perfect Clean" Fiber Textiles

3.3 Degradation of GD on Carbon Fiber Textiles.

3.3.1 Degradation of GD on Zorflex[®] FM 100 Meso Fiber Textile.

Two peaks were observed due to ~1050 Hz P-F coupling. No change was detected after 1 day, but at 7 days all GD was gone, leaving only one peak, pinacolyl methylphosphonic acid (PMPA). The total integrated peak area decreased by one third over the week. The T₁s were ~1 s, and the peak widths increased from 400 to 800 Hz; the broad peak widths suggested absorption of the GD into the pores of the fibers (Figure 8a).

3.3.2 Degradation of GD on Zorflex[®] FM 50K Fiber Textile.

Two types of peaks were observed. The narrow peaks were due to GD in a liquid-like state on the fiber textile, whereas the broad peaks were due to GD absorbed in pores and shifted upfield. Four narrow peaks were due to two diastereomers of GD, with ~1050 Hz P-F coupling. The broad peaks at 25 hr had ~1050 Hz P-F coupling, indicating

that GD was still present and absorbed in the pores. At 2 and 3 days, some of the GD had reacted; at 7 days all was gone, leaving only one peak, PMPA (Figure 8b). The PMPA was confirmed by extraction with acetonitrile followed by LC/MS.

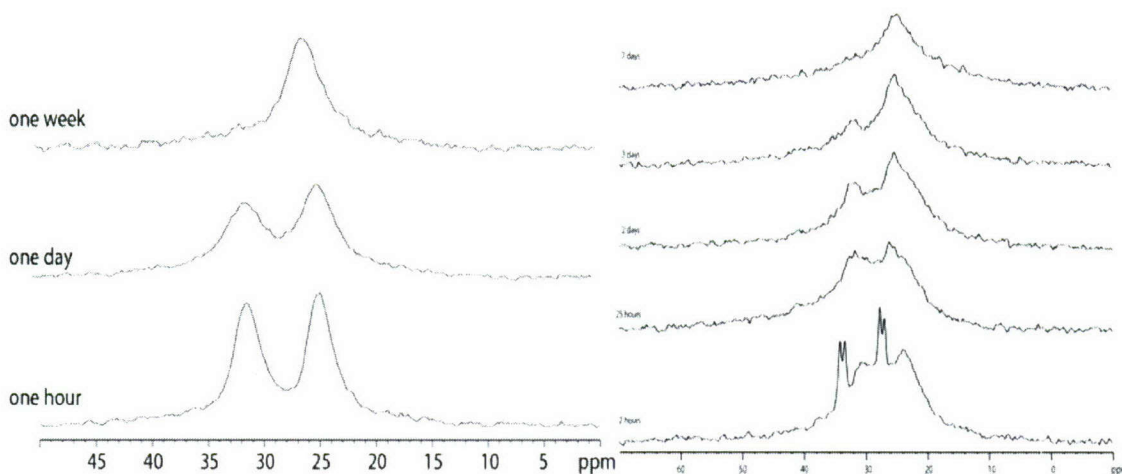


Figure 8. Degradation of GD on (a) Zorflex[®] FM 100 Meso and (b) Zorflex[®] FM 50K Fiber Textile

4. DISCUSSION

4.1 Absorption and Molecular Volumes.

During the course of this work, it was observed that, on average, each mole of ^{31}P gave about 230 cm for the total integrated peak area's height, regardless of the source of the ^{31}P . The GD eventually gave broad peaks (indicating absorption) on both the mesoporous FM 100 and microporous 50K fiber textiles, although penetration took longer on the microporous 50K fiber textile. The VX gave broad peaks, indicative of absorption on the mesoporous FM 100 fiber textile but not the microporous 50K fiber textile. This was attributed to the inability of the larger VX molecule (0.439 nm^3 , compared to 0.296 nm^3 for GD) to enter the more prevalent smaller pores of the 50K fiber textile compared to the 100 Meso fiber textile (see Table 1).

The VX on the Zorflex FM 100 Meso did not give the full expected ^{31}P integral, although the value obtained for GD was as expected. The reasons for this are not known.

4.2 Reaction Rates and Products.

The reaction rates of the VX on the fiber textiles were compared to the rate on sand (Table 4); the rates for VX loss are similar to each other, although the products differ. The product formed on the fiber textiles from VX is, unfortunately, toxic "pyro"; this molecule is known to degrade to non-toxic EMPA with the addition of water.

The order of the reaction on the FM 100 Meso fiber textile is zero – this may imply that the fiber textile itself is participating in the reaction.

The reaction rates of the HD in the fiber textile are faster than on ambient sand, concrete, asphalt, and limestone, and competitive with moist sand, concrete, asphalt, and limestone.

The fiber textiles are known to retain atmospheric moisture. Apparently this moisture is able to react with the HD and GD but is insufficient to produce EMPA from “pyro”.

Blank

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